n/*p*-Type Transparent Conductors

R. Chang[+], T. Marks[+*], T. Mason[+], and K. Poeppelmeier[*]
Department of Material Science and Engineering, and the Department of Chemistry
Northwestern University, Evanston, Il 60208

ABSTRACT

An integrated bulk materials synthesis, thin-film, and characterization of known and new transparent conductors is in progress. A study of the optical gap and thermopower in the $Cd_{1+x}In_{2-2x}Sn_xO_4$ solid solution reveals a change from normal to inverse spinel for x = 0 → 1 which gives rise to a marked decrease in the fundamental gap; different behavior than in corresponding films. Pulsed laser deposition growth of epitaxial $Cd_{0.975}Sn_{0.025}O$ films on MgO (111) possess phenomenal electron transport properties; σ_{max} = 42,000 S/cm and μ = 608 $cm^2/V\cdot s$. Homogeneously doped $Cd_{0.95}In_{0.05}O$ films grown on float glass exhibiting σ_{max} = 16,000 S/cm and μ = 70 $cm^2/V\cdot s$ with a broader transparency window than ITO were grown by metal-organic chemical vapor deposition. A new low temperature hydrothermal synthetic technique has been successfully applied to delafossite materials including $CuAlO_2$. Samples of *p*-type $CuAlO_2$ prepared by this method have conductivities 3 orders of magnitude greater than those prepared by conventional high-temperature solid-state techniques.

1. Introduction

Substances exhibiting high electrical conductivity, optical transparency, and which can be grown efficiently as thin films are critical for next generation photo-voltaics, energy-efficient windows, flat panel displays, organic-LEDs, and many other opto-electronic applications[1]. Transparent conductors such as ITO and F-doped SnO_2 have been used and studied extensively but are insufficient for many future applications[1]. The best *p*-type materials have much poorer properties than their *n*-type analogues[2,3]. The development of industrially useful *p*-type materials would allow flexibility in device structure design and provide opportunities for new technologies. Thus a fundamental understanding of the way crystal and electronic structure, film microstructure, and doping level affect TCO carrier mobilities and optical transparencies is needed as a guide to discovering new materials. To this end a collaborative bulk and thin film effort has commenced and the results thus far are summarized below.

2. Hydrothermal synthesis of p-type delafossites[4,5]

The first single-step hydrothermal synthesis route for *p*-type TCO copper delafossites, including $CuAlO_2$ and $CuGaO_2$ has been demonstrated. The complete $CuAl_{1-x}Ga_xO_2$ solid solution series, which is not accessible by any other known method, has also been achieved. The resulting powders exhibit superior conductivity and thermal stability to conventionally prepared materials, with significant oxygen intercalation into the structure, as evidenced by TGA and X-ray diffraction Rietveld analysis (corresponding to hole concentrations as high as 0.24 per Cu). The universality of this synthetic route can be demonstrated in that samples of $CuFeO_2$ and $CuLaO_2$ have also been prepared.

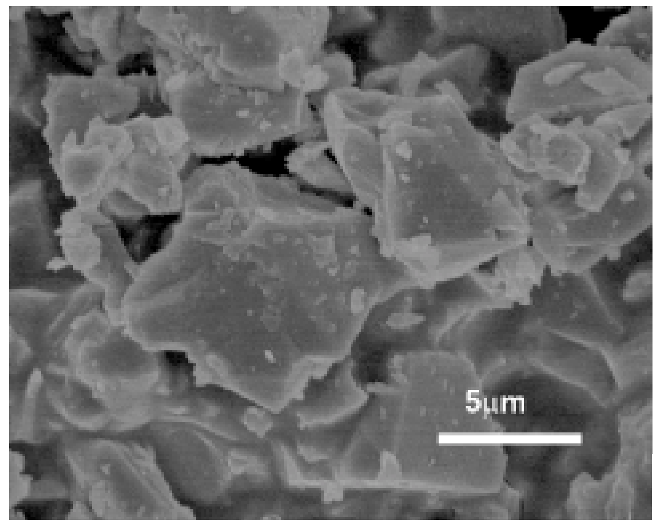

Figure 1. SEM image of hydrothermally grown polycrystalline $CuAlO_2$.

3. The $Cd_{1+x}In_{2-2x}Sn_xO_4$ solid solution[6]

The bulk subsolidus phase relations were determined in the system CdO-In_2O_3-SnO_2 at 1175°C. Among others, a spinel solution $Cd_{1+x}In_{2-2x}Sn_xO_4$ (0<x<0.75) was discovered. The cation distribution in the spinel solution evolves from primarily normal $CdIn_2O_4$ to inverse Cd_2SnO_4 as two octahedral In^{+3} cations are replaced by one Cd^{+2} and one Sn^{+4} cation. The solution terminates near x=0.75, perhaps because there is no longer sufficient octahedral In^{+3} present to reduce short-range order effects between Cd^{+2} and Sn^{+4}. The electrical and optical properties of the spinel solution were investigated in bulk and thin-films. The optical gaps in thin films increase from 3.5 eV for 0<x<0.2 to 3.7 eV for 0.2<x<0.70 while bulk specimens show a decrease from 3.0 eV for 0<x<0.2 to 2.8 eV for 0.2<x<0.70. The optical gap decrease with increasing x in bulk specimens of the spinel solution stems from the decrease in the fundamental band gap related to a change in the cation distribution between normal $CdIn_2O_4$ and inverse Cd_2SnO_4. The optical gap increase with increasing x, as observed in thin-film spinel specimens, stems from an increase in Burstein-Moss shift with increasing x that offsets the drop in fundamental band gap with increasing x. Since the fundamental band gap can be tuned in the spinel by changing composition or synthesis temperature, an additional degree of freedom useful in tuning the optical window is gained.

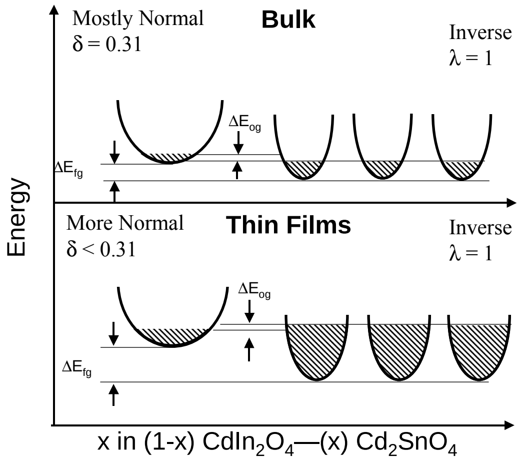

Figure 2. Qualitative schematic of the change in conduction band curvature, level of degeneracy, and fundamental band gap along the solution $Cd_{1+x}In_{2-2x}Sn_xO_4$ in bulk and thin film specimens. (ΔE_{og}= difference in optical gap, ΔE_{fg} = difference in fundamental band gap).

4. MOCVD of $Cd_{1-x}In_xO$ films on float glass[7]

$Cd_{1-x}In_xO$ films having a simple cubic crystal structure have been grown by a straightforward metal-organic chemical vapor deposition process utilizing a simple Cd-coordination complex, $Cd(hfa)_2(TMEDA)$, and $In(dpm)_3$ as precursors. The carrier concentration of the films increases with the increased doping, which results in increased electrical conductivity and bandgap energy due to the Burstien-Moss Shift. The x = 0.05 film conductivity of 17,000 S/cm, carrier mobility of 70 cm^2/Vs, and visible region optical transparency window considerably exceed the corresponding parameters for commercial indium-tin oxide (ITO).

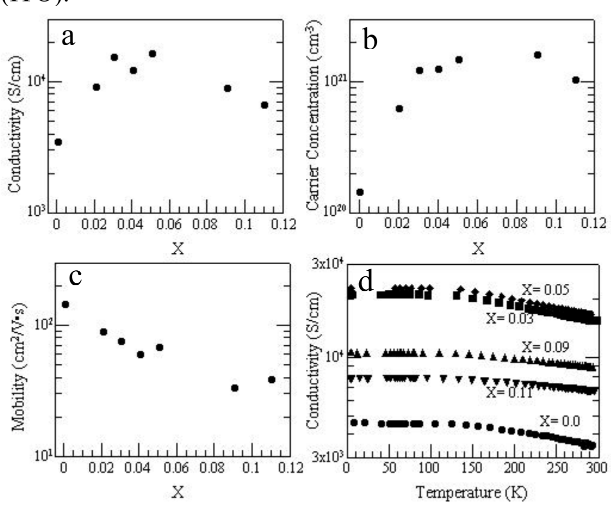

Figure 3. (**a**) Plot of electrical conductivity (σ), (**b**) carrier concentration (n), (**c**) and carrier mobility (μ), as a function of In doping content (x) for a series of $In_xCd_{1-x}O$ films. (**d**) Electrical conductivity (σ) as a function of temperature.

5. PLD of epitaxial CdO on MgO(111)[8]

Epitaxial growth of $Cd_{1-x}Sn_xO$ thin films can be achieved on MgO (111) utilizing pulsed laser deposition. The carrier concentration of the films increases with the increase of doping, which results in increased electrical conductivity and bandgap energy. A maximum conductivity of 42,000 S/cm with a maximum mobility of 609 $cm^2/V\cdot s$ is achieved when the epitaxial film is doped with 2.5% Sn. Above this optimum doping concentration, crystalline defects start to deteriorate the film electrical properties. Carrier concentrations are found to be essentially independent of the Hall measurement temperature, while mobilities and conductivities initially increase with decreased temperatures. Both grain boundary scattering and ionized impurity scattering influence the mobility behavior for these $Cd_{1-x}In_xO$ films.

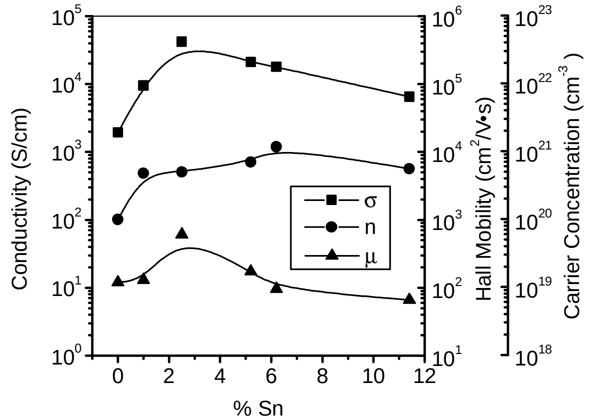

Figure 4. Relationship between Sn doping and electrical properties of CdO thin films: conductivity (■), Hall mobility (▲) and carrier concentration (●).

6. References

(1) Ginley, D. S.; Bright, C.; eds. "Transparent conducting oxides" *MRS Bull. 25*,**2000,** Articles therin.

(2) Duan, N.; Sleight, A. W.; Jayaraj, M. K.; Tate, J. "Transparent p-type conducting CuScO2+x films" *Appl. Phys. Lett. 77*,**2000,** 1325-1326.

(3) Kawazoe, H.; Yasukawa, M.; Hyodo, H.; Kurita, M.; Yanagi, H.; Hosono, H. "P-type electrical conduction in transparent thin films of CuAlO2" *Nature 389*,**1997,** 939-942.

(4) Shahriari, D. Y.; Barnabe, A.; Mason, T. O.; K.R.Poeppelmeier "A High Yield Hydrothermal Preperation of CuAlO2" *Inorg. Chem.*,**2001,** (In Press).

(5) Shahriari, D. Y.; Barnabe, A.; Mason, T. O.; K.R.Poeppelmeier "Commercial-Scale Synthesis of p-type TRansparent Conductors" *Provisional Patent # 60/281,211*,**2001**.

(6) Kammler, D. R.; Mason, T. O.; Young, D. L.; Coutts, T. J.; Ko, D.; Poeppelmeier, K. R.; Williamson, D. L. "Comparison of Thin Film and Bulk Forms of the Transparent Conducting Oxide Solution Cd1+xIn2-2xSnxO4" *J. Appl. Phys.*,**2001,** (In Press).

(7) Wang, A.; Babcock, J. R.; Edleman, N. L.; Metz, A. W.; Lane, M. A.; Asahi, R.; Dravid, V. P.; Kannewurf, C. R.; Freeman, A. J.; Marks, T. J. "Indium-cadmium-oxide films having exceptional electrical conductivity and optical transparency: Clues for optimizing transparent conductors" *Proc. Natl. Acad. Sci. U. S. A. 98*,**2001,** 7113-7116.

(8) Yan, M.; Lane, M.; Kannewurf, C. R.; Chang, R. P. H. "Highly conductive epitaxial CdO thin films prepared by pulsed laser deposition" *Appl. Phys. Lett. 78*,**2001,** 2342-2344.